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Development of ecofriendly/biodegradable lubricants: An overview

Ponnekanti Nagendramma*, Savita Kaul

Council of Scientific and Industrial Research – Indian Institute of Petroleum, Bio Fuels Division, Dehradun 248005, India

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ABSTRACT

Synthetic and vegetable oil based esters offer the best choice in formulating environment friendly lubricants. In the present review an attempt has been made to highlight some recent developments in the area of biodegradable synthetic ester base stocks for formulation of new generation lubricants including the efforts made so far at the author's laboratory in this direction. The developed products find applications in automotive transmission fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids, industrial gear oils, neat cutting oils and automotive gear lubricants either alone or in formulations.

Contents

* Corresponding author. Tel.: +91 135 2525924; fax: +91 135 2660202.
E-mail addresses: satya1008@hotmail.com, nagendra@iip.res.in (P. Nagendramma), skaul@iip.res.in (S. Kaul).

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1. Introduction

The history of synthetic lubricants began before the internal combustion engine existed. In 1877, the first synthesized hydrocarbons were created by Friedel and Crafts using aluminum tri chloride as the catalyst. In 1937, the first synthetically manufactured product was based on olefin polymerization. Zurich Aviation Congress also took interest in ester based lubricant technology and thousands of esters were evaluated in Germany between 1938 and 1944. Ester lube base stocks were developed by the United States Naval Research Laboratory in the early 1940s and synthetic lubricants were strictly used in military and industrial applications. Before synthetics were created, vegetable oils made from castor beans and rape seed were used. Britain used diesters in turboprop engines because of its good extreme temperature performance. Later, various synthetic formulations were developed until mid 70s. AMSOIL developed the first 100% synthetic based engine oil to pass the American Petroleum Institute's sequence tests and achieve API qualification in 1972. Mobil Oil marketed its first synthetic based engine oil in the United States in 1975. AMSOIL also developed synthetic diesel oils, two-cycle oils, transmission fluids and gear lubes. Petroleum giants Mobil, Quaker State, Castrol, Valvoline and Pennzoil have all come out with synthetic alternatives to their conventional oils. Since then, almost every major company has introduced a synthetic or semi-synthetic variant [1–3].

1.1. Synthetic lubricants

In recent years pollution and environmental health aspects have become increasingly important as public issues. In the area of lubrication, the concern is to focus on the issues related to large proportion of lubricants lost in environment. The break down products are potential threats to the environment. Water and soil are contaminated directly by loss lubrication system while the air is affected by volatile lubricants or lubricants haze. The increased environmental awareness is a primary driving force for the new technological developments. Therefore biodegradable synthetic lubricants used in environmentally sensitive areas have been extensively explored [4].

One of the biggest challenges is the development of universal biodegradable base stock that could replace mineral oil base stocks is the new generation lubricants. From the better performance point of view these should be friendly to the environment and be eventually biodegradable [5].

In general, three types of base fluids find application in formulation of biodegradable, environment friendly lubricants. These are mineral oils, vegetable oils and synthetic lubricants. Synthetic lubricants have been used for many years and before their development vegetable oils were used as main lubricants. Later on various synthetic esters were developed during World War II, which were used as lubricants for many years even though their cost was very high. However, the desire for lubricants to perform over increasing temperature ranges especially for military and aero engine requirements has stimulated the development of synthetic lubricant technology [6].

In contrast to mineral base oils, the nature of which to a large extent is determined by the crude oil source, synthetic lube oils are manmade through chemical combination of low molecular weight components as building blocks to form high molecular weight compounds. Their molecular structure can be planned and controlled with predictable properties. The choice of base fluids is usually the result of their performance characteristics that are not obtainable with mineral oils. These fluids offer some major advantages but have some disadvantages as well.

Today, approximately 80% of the base stocks used worldwide in synthetic lubricants fall into the generic groups, such as synthesized hydrocarbons (~50–55%) and organic esters (~25%). Other categories include polyglycols (~10%) and phosphate esters (~5%) [7].

The synthetic lubricants, because of their eco friendly characteristics, are now making a big impact and around 60 end uses have been commercialized for automotive industrial functional/process fluids and aviation applications which include military requirements as well. Esters including phosphate esters, polyalkylene glycols, vegetable oil based products, polyalphaolefins (PAOs), alkylated aromatics, and polybutenes will dominate the market among synthetics [8].

1.2. Synthetic esters

Within the realm of synthetic lubrication, a relatively small but still substantial family of esters has been found to be very useful in severe environment applications. Esters have been used successfully in lubrication for more than 50 years and are the preferred base stock in many severe applications. For example, esters have been used exclusively in jet engine lubricants worldwide for over 40 years due to their unique combination of low temperature flow ability with clean high temperature operation [9].

Synthetic esters have been used as base fluids in lubricants for years, though their broader acceptance has been mainly hindered by their high price. According to Mang, ester chemistry offers so many possibilities that 90% of all lubricants could be produced with rapidly biodegradable esters without any loss of technical performance. Compared to mineral base oils, some technical characteristics such as thermal stability could be greatly improved.

Synthetic polyol esters are used as environmentally acceptable base fluids in high performance lubricants. A very good low temperature behaviour, high thermo-oxidative stability of some types, very high viscosity index, good anti wear and low evaporation properties have led to their use in many lubricants. Compromise between viscosity, volatility and cost influences the choice of base stocks for their effective ecofriendly formulations.

Esters are generally competitive with mineral oils. This gives them advantage that they can be blended with mineral oils to boost

this performance. Most additive technologies are based on mineral oils and hence this technology is applicable to esters also. This provides synthetic esters great flexibility while blending with other oils gives unrivalled opportunities in balancing the cost of a lubricant blend against its performance.

Esters are synthesized from relatively pure and simple starting materials to produce predetermined molecular structures designed specifically for high performance lubrication. Synthetic ester base stocks are thermally and oxidatively stable, have high viscosity indices, and lack the undesirable and unstable impurities found in conventional petroleum based oils [10].

1.3. Physico chemistry of esters

Physico chemistry of esters depends upon the balance between hydrocarbon moiety and ester group(s). Hydrocarbon chain length reflects in viscosity, viscosity index and compatibility while the pour point, oxidation and biodegradability are reflected by the extent of branching. Number of ester groups reflects in compatibility and esters acid number i.e. stearic hindrance reflects in thermal stability and hydrolytic stability.

Presence of ester group means polarity, which reflects in evaporation, lubricity and solvency. So in comparison to mineral oils, many esters have a series of technical advantages, such as natural high VI (over 160), low temperature properties (good cold flowing), pour point $<-30\,^{\circ}$C, low evaporation losses and good thermal stability i.e. high temperature properties, hydrolytic stability, good anti-friction and anti-wear characteristics, high flash point ($>260\,^{\circ}$C) compatibility and biodegradability. It has been shown that fundamentally possible types (mono, di-, poly- and complex esters) have acceptance for biodegradable lubricants primarily for cost reasons.

Studies on synthetic lubricants showed that esters from polyols, diols, triols and tetrols have been synthesized by using catalysts: solid acids [11], sulfuric acid [12], p-toluene sulfonic acid [13], tin, Zr, Ti, alcolates, carboxylates, chelates [14] and tetra alkyl titanate alkylene earth metals [15] as catalyst. These processes are quite cumbersome and yield products which require continuous monitoring and are of somewhat inferior quality base oils with significant acidity and charred products. However, some processes are reported using mordenite zeolite, LD 412 solid acid and cation exchange resins [16] as catalyst.

In the present review an attempt has been made to highlight current status of ecofriendly/biodegradable lubricants for formulation of new generation lubricants. At the author's laboratory the developed ecofriendly/biodegradable synthetic lube base stocks have been evaluated for application in automotive transmission fluids, metal working fluids, cold rolling oils, fire resistant hydraulic fluids and automotive gear lubricants either alone or in blends.

2. Why biodegradable lubricants

To initiate and boost the use of biodegradable products, government incentives and mandatory regulations are needed to put pressure on the industries that release lubricants into the environment. Several countries are awarding environmental seals, which are nothing but the environmental acceptability eco-labelling schemes. The first seal was awarded by Germany by the name as "Blue Angel". Similarly "White Swan", "Green Cross" and "Ecomark" are the environmental seals of Scandinavia, USA, and Japan and India, respectively. These eco labelling schemes include ecological test requirements, prohibitions and manufacture's declarations which often differ and are being continually updated [22].

2.1. Available biodegradable lubricants

Currently, there are five biodegradable base stocks of some significance. These are the

- highly unsaturated or high oleic vegetable oils (HOVOs),
- low viscosity polyalphaolefins (PAOs),
- polyalkylene glycols (PAGs),
- dibasic acid esters (DEs),
- polyol esters (PEs).

2.2. Vegetable oils (HOVOs)

These oils are mainly triglycerides. The glycerol fragment contains three hydroxyl groups esterified with carboxyl groups of fatty acids. Excess of saturated long chain fatty acids leads to poor low temperature behaviour, while excess of certain poly unsaturated fatty acids leads to unfavorable oxidation behaviour and resination at high temperatures. Even very long mono unsaturated fatty acids worsen the low temperature behaviour. The triglyceride structure gives these esters a high natural viscosity (and viscosity index) and is also responsible for structural stability over reasonably operating temperature ranges. The flash point is high, which correlates to a very low vapor pressure and volatility, thereby reducing or eliminating potential hazards during use. Even so, they have poor oxidative stability as compared to mineral oils and in general they cannot withstand reservoir temperatures over $80\,^{\circ}$C. However, the use of appropriate antioxidants can combat this. These oils are also less hydrolytically stable, foam more and have lower filterability than comparable mineral oils. Thus vegetable oil based products are ideally suited to applications such as saw mill blade or chain drive lubrication where the lubricant is used on a "once through" basis and where low toxicity is required. They are also well suited for use in low to medium pressure hydraulic systems or lightly loaded gear drives where the operating temperature does not normally exceed $71\,^{\circ}$C and where there is little chance of water ingress or high contamination [18,19].

2.3. Polyalphaolefins (PAOs)

The biodegradable PAOs are the low molecular dimers to tetramers. This results in undesirable high volatility characteristics for the fluids. However, the low molecular weight turns into a benefit at low temperatures where PAOs demonstrate excellent performance. They also have a tendency to shrink rubber seals, as opposed to other base stocks, and make good blending stocks. The absence of polarity leads to problems of additive acceptability, but on the other hand, results in excellent hydrolytic stability. Oxidative stability of antioxidant containing PAO is very comparable to petroleum based products due to the absence of double bonds or other reactive functional groups. PAOs are an attractive option for biodegradable lubricants to water, especially for low temperature applications. So these are finding increased use as hydraulic and engine oil, particularly in cold climate applications and where hydraulic pressures are increasing (>7000 psi). These oils are also finding selected use as gear lubricants due to their ability to provide lower operating temperatures and their lower coefficient of friction, both of which help to reduce wear. These products are generally compatible with mineral oils and as a result there is no requirement of extensive flushing prior to conversion unless required by these certain sealing materials, causing shrinkage and hence initial leakage [17].

2.4. Polyalkylene glycols (PAGs)

Polyalkylene glycols are produced by polymerizing ethylene oxide and propylene oxides or their mixtures. Instead of having mainly hydrocarbon backbone, the molecules have alternating ether linkages, which result in high polarity of the material. Solubility of organic additives is often problematic in PAGs, as is miscibility with conventional petroleum based lubricants. A high degree of polarity also provides increased solubility in water which is advantageous to a biodegradable fluid but detrimental to many lubricant applications because it tends to become contaminated with moisture rapidly. However, for applications such as biodegradable fire resistant fluids PAGs are often the best option [17].

2.5. Diesters (DEs)

The diesters are composed of dicarboxylic acids (such as adipic acid) esterified with alcohols produced from hydroxylated petroleum fractions. Their molecular weight is high enough to disregard volatility problems and ester linkages deliver high solubilising power. Branching in the alcohol fragments leads to very good low temperature performance but is probably a primary factor why diesters score low on tests for ultimate biodegradability. In addition, their ester linkage is not hindered sterically to restrict hydrolytic decomposition. Despite all that diesters enjoy increasing demand as base stocks for biodegradable hydraulic fluids with extended drain intervals and are mixed with PAOs in a number of synthetic lubricants that possess excellent properties. These are excellent biodegradable lubricants for compressors and turbines. Diester fluids may have a negative effect on certain varnish or paint surfaces, due to their exceptional solvency and detergency, so it would be wise to remove the paint from any internal contact surfaces, such as the reservoir prior to conversion to biodegradable diester lubricant. As they negatively affect the sealing material, fluorocarbon seals should be considered for these applications [18–20].

2.6. Polyol esters (PEs)

Polyol esters are composed of fatty acids attached to an alcohol which does not contain a hydrogen atom on the β-carbon atom. In case of saturated fatty acids this leads to very high oxidative stability, satisfactory hydrolytic stability, relatively high biodegradability and excellent low temperature performance. However, molecular weight of polyol esters often results in high viscosities. There are a number of manufacturers of different types of polyol esters, and some of them may contain unsaturation. For example, polyol oleates are polyols designed for lower viscosity. However, the presence of double bonds results in poorer oxidative stability. Other types of polyols deliver a high performance, but do not have satisfactory biodegradability. Principal chemical structure of the polyol ester must be assessed before considering it for a particular lubricating application [21].

3. Development of biodegradable high performance hydrocarbon

3.1. Base oils

The lubricant industry's toughest challenges are performance; environmental compatibility and cost concern for the environment have been shown by the continuous developments and research on synthetic lubricants to minimize the way our daily activities impart on the environment. Today some manufacturers are blending diesters with PAOs to form base oils which are biodegradable, have good solubility, resist oxidation and have good temperature viscosity characteristics. Others are blending synthetic diesters with canola oil to provide similar results. In any way, maximizing biodegradability and minimizing ecotoxicity of lubricants to reduce environmental impact has been a primary driving force in product formulation in recent years.

These days, each and every forum is mainly focusing on the development of energy efficient products and on conserving the petroleum and environment by furthering the activities and research in developing the much needed eco-friendly and biodegradable products.

The choice made will depend upon the lubricant application, balancing cost constraints against technical and environmental targets, particularly emphasizing such features as biodegradability and recyclability. Most lubricants are based on combinations of mineral oils, with the additions of synthetic fluids as appropriate for higher levels of performance. Technically the performance of esters exceeds that of conventional mineral oils in most areas, excluding hydrolytic stability, wear protection and compatibility with some seal materials. However, ester based lubes are typically more expensive than their mineral based counterparts. On the other hand, performance warranty and environmental standards for industrial motors, engines and equipments are causing world demand for high performance lubricants. As a result, a switch to alternative base stock is required to meet current requirement for environmentally compatible lubricants. The two primary classes of biodegradable lubricants, vegetable oils and synthetics have been described.

Vegetable oils have many of the advantages of esters at a relatively lower cost. They have high VI, good lubricities and extreme pressure properties, low volatilities, and additive and mineral oil compatibility. Because of their poor thermal oxidative and hydrolytic stability they have not found wide usage in lubricants [22,23].

3.2. Suitability of base stocks for biodegradable lubricants

Lubricant manufacturers are facing a number of challenges in preparing for an anticipated boom in demand for biodegradable lubricants and hydraulic fluids. The effort promises major benefits in providing users with a new generation of environment friendly products.

Awareness is growing on the advantages of biodegradable lubricants. In order to develop these eco-friendly base stocks, a number of approaches are being studied. As described previously five types of biodegradable base stocks are currently available to the manufacturers who want to produce ecofriendly lubricants. For each of them, it must be considered whether biodegradability is a realistic concept, technically feasible, environmentally necessary and cost efficient.

Vegetable oil based lubricants based on renewable sources, such as corn, soy beans and rape seed, easing dependence on foreign sources of imported petroleum. They have less potential toxicity and degrade more readily in the environment. Biodegradable lubricants and hydraulic fluids based on these will be widely available in United States. Genetic engineering efforts yield vegetable oils with better lubricating properties. These include genetically modified corn and soybean oils with high oleic content that enhances oxidation stability [24].

Synthetic lubricants whether synthetic hydrocarbon, organic ester, or other chemistry all face the same daunting problem. Mineral oil based lubricants are cheap and plentiful. So, the question arises how to convince industrial users to pay triple, quadruple or even scores more per pound for a synthetic product. One can justify it from the stand point of performance, warranty costs, avoiding early failure of the part, etc. despite evidence that costs can be cut by switching to synthetic lubricants [25]. Their needs are so simple

and petroleum oils and greases are so cheap that synthetics cannot compete for these applications, despite a wide spread impression among industrial users that in general, synthetic lubricants protect better, last longer and out perform their conventional counterparts.

Thus the conventional lubricants are strongly entrenched. However, the upcoming finished lubricant quality specifications in view of their improved performance to meet future's stringent environmental regulations are the main driving force for new technological developments.

3.3. Biodegradable lubricants

In Western Europe several biodegradable gasoline engine oils already have been introduced in the market. Most of these formulations consist of about 50:50 mixtures of esters with PAOs or hydro cracked oils and conventional additives. But further environmental optimization is possible if the ester contents are increased especially in terms of biodegradability and volatility. Test results and practical experience with an engine oil based on synthetic carboxylic acid esters (SAE 5W/30) demonstrated the advantages of such lubricants, e.g. low particulate emissions, reduced oil consumption, high engine cleanliness (low deposition) and biological degradability [26].

Concern for the environment has been shown by the continuous developments and researches on synthetic lubricants to multimise the way our daily activities impact on the environments. The lubricant industry's toughest challenges are performance, environmental compatibility and cost. It can only be done with the service, research and leading edge products most of which are based on natural renewable/synthetic raw materials. Vegetable oils as base fluids for “bio sphere safe” lubricants have proven to be a sound solution to the past of the problem that we face now and in future. They provide good performance, low impact on the environment and credibility in the public eye.

There are a lot of different vegetable oils, but not all can be used for high performance lubricants. There are technical, logistic and cost barriers. It is very difficult to anticipate that up to what extent the mineral oils will be replaced by the vegetable oils (% world consumption) but approximately one can guess it up to 30% in several years. In Europe, rape seed oil has been found to be the best. It is locally produced agricultural crop which is currently in other production and possesses excellent tribological and environmental properties; compatibility with equipment seal elastomers is also excellent. In fact with the exception of thermo-oxidative stability, it is comparable in performance with best of synthetic base stocks. The role of vegetable oil other than rape seed in future as a replacement of mineral oil depends on where the material is grown. Palm oil, castor oil and other oils have also been investigated in different parts of the work emerging a future for these products.

In India nearly a million tonnes of low priced fatty oils with superior lubrication and VI characteristics are available from seeds of plants growing wild out in forest. These oils meet most of the characteristic of a high performance energy efficient lubricant except for pour points, high to very high VI, low viscosity, out standing friction wear and lubricity characteristics and impart thermo oxidative stability. The objective should be to achieve those desirable characteristics without involving steep hike in the cost of producing such derivatives.

The aim of study eventually should be to transform low priced fatty oils into high performance, energy efficient, long life environment friendly lubricant components for automotive and gear oils at comparable cost. A number of alternative products can be obtained by simple chemical transformation of vegetable oils. The antiwear and friction reducing properties almost are twice as good as those of the mineral oils which signifies their energy efficient performance or in other words, one can say that demand for lower volatility, larger drain intervals and improved high and the temperature performance has led to a significant increase in the use of UHVI synthetic base oils, all of which require the use of less additives [27,28].

Simply comparing the price of different synthetics with that of conventional lubricants can be misleading. The synthetics may require less frequent application, for example, or it might have higher disposal costs. So the factors such as machine down time, unscheduled repairs and disposal costs should also have to be considered to get real group or the price/benefit relationship [29].

For every type of synthetic lubricant, there is a balancing act between desirable and undesirable characteristics. So when considering a synthetic oil, it is suggested putting a value as each performance characteristic that is needed – including price – and then weighing all the advantages and disadvantages of the lubricant in the users' own specific application.

3.4. Future challenges

As industry moves forward into the 21st centuries, It can be anticipated that equipment manufacturers, consumers and regulatory agencies will continue to place ever-increasing demands on the performance features required of lubricants. It is expected that demands placed on the lubricant will continue to increase with the severity of operating conditions. While the specific details and rates of change are different for various applications, high loads, speeds and increase drain intervals are almost universal trends. In some cases, the concept of fill for life has been raised and indeed, in some applications this has essentially achieved through the use of synthetic lubricants for initial fill of equipment. There will also be a sustained drive to protect the environment that will continue to favor the use of less toxic, more biodegradable and superior energy-conserving products.

4. Current status and lubricant market

4.1. The total lubricant market

The global lubricant market in the past 10 years has undergone dramatic changes. The industry has witnessed over all flat demand, sharp shifts in consumption, increased competition and greater pressure on profits. World lubricant demand has remained flat around 35 million tonnes/year since 1991. The same holds true for the EU where the total lubricant demand of about 5.3 million tonnes/year has stayed unchanged since 1982. Germany is the largest national market for lubricants in Europe and ranks fifth in global terms with a total lubricant consumption (2.5 million tonnes/year; that is 47%) while industrial lubricants account for 1.7 million tonnes/year (32%), marine and aviation lubricants for 0.5 million tonnes/year (9.4%) and process oils for 0.6 million tonnes/year (11.3%). Hydraulic oils make up the biggest part of industrial oils and are the second most important group of lubricants after automotive lubricants accounting for about 15% (0.75 million tonnes/year) of the total lubricant consumption [30,31].

In 2004, 37.4 million tonnes of lubricants were consumed worldwide. 53% automotive lubricants, 32% industrial lubricants, 5% marine oils and 10% process oils. Of total industrial lubricants, 37% were hydraulic oils, 7% industrial gear oils, 16% metal working fluids and 9% greases [32].

Looking at the development of the global lubricant market, disregarding marine oils, a clear continuous recovery of worldwide demand can be witnessed since 2003, to 37.2 millions in 2007. Lube consumption in Western Europe was flat in 2007, compared to the previous year, while all other regions generated positive volume growth rates between 1.5% and nearly 2%. Remarkably, the highest

rate growth in 2007 was achieved in the middle east region. Overall, the increase in global lubricant consumption from 2006 to 2007 amounted to 0.8%. So far only limited data on the market in 2008 is available. However total lube consumption in the major industrial nations like United States, Japan, Germany, France and Italy decreased by close to 3% through the first three quarters. When it comes to country ranking the US continues to be the world's largest lube market, followed by Japan and China. Together the top 20 lubricant markets in 2007 accounted for nearly 75% of worldwide lube consumption. In the past 10 years overall, in volume terms Europe and the Americas together lost what Asia-Pacific and rest of world gained, and these latter regions now share close to 44% of the global lubricant market. Fuchs estimated that in the next 10 years the global lubricant market will grow at a compound annual growth rate of 1–41 million tonnes, further driven by increasing demand in emerging markets. To round out the global perspective, today the top 20 lubricant manufacturers hold around two-thirds of the world's land based lubricant demand [33].

Global top 20 lubricant manufacturers [36].

Shell	Great Britain/The Netherlands
Exxon Mobil	USA
BP	UK
Chevron	USA
Petro China/Sinopec	China
Lukoil	Russia
Total	
Fuchs	Germany
Nippon Oil	Japan
Idemitsu	Japan
Valvoline	USA
Conoco Phillips	USA
Petrons	
CPC	Taiwan
Petramina	
PDVSA	Venezuela
Repsol	Spain
SK Corp	
Indian Oil	India

Source: Fuchs Strategic Marketing.

The world's largest manufacturers of finished lubricants are listed below.

World ranking of the largest manufacturers of lubricants [34–36].

Shell	Great Britain/The Netherlands
Exxon Mobil	USA
BP	UK
Petro China/Sinopec	China
Chevron	USA
Lukoil	Russia
Fuchs	Germany
Nippon Oil	Japan
Valvoline	USA
Idemitsu	Japan
Conoco Phillips	USA
CPC	Taiwan
PDVSA	Venezuela
Repsol	Spain
Indian oil	India
Agip	Italy
Yukos	Russia

4.2. International status

Worldwide there are 1700 lubricant manufacturers ranging from large to small. Some 300 of them are located in Europe. Besides there are approximately 380 blending and packaging plants and 90 grease manufacturer's in Europe. These are mainly vertically integrated petroleum companies whose main business is the discovery, extraction and refining of crude oil (ExxonMobil, Shell, BP Castrol, Total, etc.). Lubricants account for only a very small part of their business. The 1200 independent lubricant companies mainly concentrate on the manufacturing and marketing of lubricants. While the large companies focus on engine, gear and hydraulic oils. Less than 2% of lubricant manufacturers produce more than 60% of the global lubricant volumes [30].

Companies like The Lubrizol Corporation of Ohio, US, research centers like the University of Northern Iowa's National Ag-Based Lubricants (NABL) Center, and commercial companies like Environmental Lubricants Manufacturing, Inc. (ELM), in Iowa, US, introduced various greases, metal working fluids and hydraulic fluid products made of vegetable oils. The success of creating stable hydraulic oils with vegetable oil further led to the development of other lubricant products including metal working oils and coolants, as well as greases [37,38]. Esters are commercially available from companies like Texaco, Lubrizol, Henkel, Gulf Oil Company, Hatco, Amsoil, Shell, Exxon Mobil, Fuchs, Becham Biolubricants, ICI Emkarate, Estimol, Castrol, Petro China/Sinopec, Lukoil, BP, Chevron, Nippon Oil, Valvoline, Idemitsu, Conoco Phillips, Repsol, Indian Oil, Agip, Yukos.

4.3. National status

In India this type of work has been done at Indian Oil Corporation [35] Faridabad, Indian Institute of Petroleum [7,15,41,54,74–77], Dehradun. Indian Institute of Chemical Technology, Hyderabad, Defense Materials and Stores Research & Development Establishment [12] Kanpur, BPCL and HPCL India.

4.4. Indian scenario

In India we are expected to consume more than 100 million tonnes per annum of petroleum products before the dawn of the 21st century and we can visualize consumptions of around 2.0 million tonnes per annum of lubricants.

IOCL whose 2008 revenues were $49.6 billion develops, produces markets and distributes lubricants and greases, which are mainly available under the SERVO brand name. The SERVO product portfolio consists of more than 500 grades intended for use in a broad array of automotive, industrial, railroad, marine and other applications. Specific products include SERVO SUPER passenger car motor oils, SERVO 2T SUPREME two-stroke engine oils, SERVO PRIDE and SERVO SKODA diesel engine oils, SERVO UNITRAC tractor oils, SERVOGEAR gear oils, SERVOGEM industrial greases, SERVOCUT.

The large scale use of two wheelers and three wheelers makes a lot of difference. Air middle distillate use currently about 35 million tonnes and is almost 10 times that of motor gasoline. Thus the Indian scenario is quite different from that in the developed world. Engine oils will continue to be the important base stocks to the extent that ∼97% are obtained from the crude oil and only 3% are synthetic which is largely due to cost consideration [35].

The large scale expansion in petroleum processing coupled with the rapid growth in the manufacture of the trucks and tractors and new generation cars, etc., is sufficient to fuel the growth of the lube base oils manufacture in India. The large scale use of middle distillates in locomotive for massive Indian railways places additional demands.

Vehicle manufacturers are under increasing pressure due to emission legislation. In order to improve the air quality, legislation will have a consider significant reductions in HC, CO and NO_x levels in case of diesel vehicles, particulate emission for both passenger cars and heavy duty engines [36].

5. Currently available commercial products

Latest literature report on biodegradable lubricants shows that some manufacturers now market environmentally acceptable biodegradable lubricants in the United States, Europe, and Asia. US patent numbers 6,278,006 August 21, 2001 [39], 6,420,322 July 16, 2002 [40], 20050150006 July 7, 2005 [41], US 6,943,262 September 13, 2005 [42], US20080293602 November 27, 2008 [43], US201001964 24, August 5, 2010 [44] disclose lot of work done on biodegradable lubricants.

Other products currently available from soybean oils include tractor transmission hydraulic fluid, industrial hydraulic fluids for process and machinery, metal working oils and coolants, food grade hydraulic fluids, chainsaw bar oil, gear lubes, compressor oil, greases, including automotive, machinery, rail curve track and food grade. Development of more than 30 viable soybean-based lubricants, grease and metal working fluid formulations including the high-performance multi-grade hydraulic fluid, brand named BioSOY™, a patented electrical transformer fluid named BioTRANS™, chainsaw bar oil called SoyLINK™, a rail curve lubricant called SoyTrak™, and Soy TRUCK™, a semi truck fifth-wheel grease has been reported by Honary [45].

Currently biobased lubricants are in operation in a number of environmentally sensitive applications such as in transformers, building elevators and machinery used in or near forests, agricultural land and waterways. Commercialized successful technologies have also been demonstrated in USA. A biodegradable soy based hydraulic fluid that has been used to operate the elevator system in the state of statue of liberty, since 2002. The other technology is soy based hot rolling lubricants used by a large aluminum manufacturing company for everything from beer cans to aircraft wing panels for hot flat rolling operations. Also at Penn state university, senior research scientists have been impleting biobased lubricants and biofuels. They made tri methylol propane or penta erythritol base fluid from vegetable oil for hydraulic fluids [46,47].

Van Rensselar [48] reveals that biobased products are being successfully applied in Europe in metal working and industrial lubricants, greases, tractor oils and hydraulic fluids. The use of biobased automotive lubricants is so far very limited because of performance issues. However, some biobased products proved to be highly efficient as lubricity additives in formulations of fuel economy engine oils and transmission fluids. As the economy recovers, technology advances and public awareness grows, more benefits of biodegradable lubes and greases will be recognized and the market will see more biobased products.

5.1. Some studies on ester based lubricant formulations

5.1.1. Vegetable oils

Mineral oil is mostly consumed as insulating oil, gear oil, two stroke engine oil, hydraulic oil, metal working fluid, greases, thinner and solvents are currently produced in India from petroleum crude oil derived lube base stocks or synthetic oils. These products from non-edible vegetable oils like neem, castor, mahua, ricebran, karanza, and linseed oils which offer better or at least same performance as petroleum or synthetic oil based products besides being less expensive [49–53].

5.2. Synthetic polyol esters

New base fluids based on synthetics have been developed to cater to the needs of high performance lubricants. As a result, synthetic fluids as a base stock have attained considerable importance in a variety of industrial and military applications. Some of the applications include engine lubricants, gear oils, hydraulic oils, compressor oils, pump and turbine oils.

Certain synthetic fluid will have to be selected and applied in spite of some of its disadvantageous properties or in other words each type of synthetic offers some strong advantages and carries some disadvantages as well. However, the use of biodegradable products in the area of hydraulic fluids, chain saw oils, compressor lubricants and metal working fluids is increasing rapidly.

There has been steady increase in the demand for biodegradable, environmentally harmless lubricants especially in ecologically responsible areas. There is a potential for developing novel biodegradable and ecologically harmless base stocks for new generation of lubricants. Before ecological aspects became part of lubricant development, ester oils were used as special lubricants for various technical reasons. The inherent biodegradability of these ester molecules offers added benefits [39,54].

Esters are normally synthesized using conventional catalysts. The catalysts are used for once through applications, have disposal problem, yield base oils with significant acidity and are not eco-friendly [40,55]. Biodegradable ester lube base stocks have been synthesized by using non-conventional, indigenous commercial catalysts. The use of non-conventional catalyst affords the derived product with negligible acidity. The process has superiority with respect to ease in handling, less reaction time, lower molar ratio of acid to alcohol, high purity, cost effectiveness because of recyclable nature and yields of the order of 95% and above. However, all the base fluids have been synthesized for the first time with ion exchange resin catalyst.

The final biodegradable ester lube base stocks were characterized by the physico-chemical analysis by using standard ASTM test methods.

Based on the viscosity index, majority of these products belong to Group III category of base oils as per API classifications. Synthetic esters are most widely used in many applications including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oil and grease formulations. On the basis of the product properties, these base fluids may find applications either alone or in blends. Based on performance evaluation the synthesized polyol esters were classified as

- automotive transmission fluids;
- metal working fluids;
- steel cold rolling oils;
- fire resistant hydraulic fluids;
- automotive gear oils.

5.3. Automotive transmission fluids

Synthetic automotive transmission fluid provides automatic transmission power steering units and hydraulic system with excellent lubricating protection and better performance, a wider temperature range, than do commercial petroleum fluids. Transmissions usually operate under severe conditions. Formulated oils provide cooling, lubrication and rust protection between moving parts. Finished biodegradable lubricant can be produced using an appropriate base stocks and suitable additives. In view of the environment sensitivity of automatic transmission fluid, two formulations which have the potential as biodegradable base stocks were prepared using commercial anti wear additives. These two formulations were compared to the commercial ATF. The results indicate that the formulation is matching with the commercial automotive transmission fluid. Salient features of these synthetic polyol esters are suitable for some applications as vegetable oils, but their better thermal and oxidative stability and lower pour points can usefully extend the scope of successful application in lubricating oil formulations. Since the finished lubricant normally consists

of 90+% base oil, the polyol base stock is surely a biodegradable product [56,57].

5.4. Fire resistant hydraulic fluids

Hydraulic fluids based on mineral oils, though having an optimum performance fail to meet toxicity and biodegradability requirements. Synthetic esters appear as promising candidates where environmental protection is of utmost importance. Products were characterized for their physico-chemical properties and evaluated for their lubrication performance. Comparison of the specifications of fire resistant hydraulic fluids of VG-22 Grade with physico-chemical characteristics of the synthesized esters indicates that they have good potential as a base stock for fire resistant hydraulic fluids.

However, the esters have low auto-ignition temperature and poor wear characteristics in comparison to fire resistant hydraulic fluids of VG-22 grade. In order to improve these characteristics the esters were blended with a commercial anti wear additive hereby showing an improvement in the wear property and also auto-ignition temperature.

From the studies, it can be correlated that the synthesized polyol esters have good potential for use as a base stock for formulation fire resistant hydraulic fluids VG-22 grade [58].

5.5. Automotive gear oils

At present mineral oil based lubricants are widely being used for all type of practical applications, but the increased environmental awareness has forced to look for alternatives for replacing mineral oils. Synthetic esters with their good lubrication properties offer a better option [59,60].

Using these esters, gear oils were formulated with commercial automotive gear oil additive package and the formulations were then evaluated along with the commercial gear oil of SAE 90 GL-4 level. Although the physico-chemical properties of the synthetic complex esters are matching with the SAE-90 multipurpose gear oil (GL-4), the tribological performance data is not meeting the specification. Therefore, all the three potential base stocks were blended with commercial EP type of automotive gear oil additive package at the recommended dosage. These three formations were evaluated for physico-chemical and tribological performance. The laboratory performance of these formulated gear oils was comparable with that of the commercial automotive gear oil (SAE 90 GL-4 level). The results indicate that the selected conventional gear oil additive package has compatibility with the synthesized complex esters also [61,62].

5.6. Metal working fluids

The synthetic polyol esters are being evaluated for lubricity performance with a view for their application as metal working fluids. The physico-chemical characteristics of polyol esters indicate that the properties are matching with the conventional base stocks. However, the saponification values of these esters are very high which is an additional benefit for improving their lubricity performance.

5.7. Steel cold rolling oils

The synthesized esters were evaluated for their physico-chemical characteristics as well as for their lubrication performance on the conventional tribo testers. Besides, with a view to see the possibility of using these esters as cold rolling oils, their lubricity characteristics were studied using indigenous test technique developed at our laboratory [63]. Conventional cold rolling oils (CROs) are used to impart lubrication at the roll work piece interface and for cooling of the rolls. CRO not only reduces energy consumption but also enhances the roll life resulting in improved product quality [64,65].

The physico-chemical characteristics of polyol esters indicate that the properties are matching with those of conventional base stocks. The saponification value of synthesized esters is very high and gives an added advantage for improving their lubricity performance. The CRO should have moderate to high load bearing capacity (LBC) and good lubricity property. The LBC is determined on 4-ball E.P. tester by IP-239 method and is represented by weld load. The lubricity property is evaluated by indigenous method. The test method consists of determination of frictional characteristics of lubricants under superficial plastic deformation conditions. Lower friction values mean better lubricity [66].

The present study indicates that the synthetic polyol, mixed polyol and complex esters have good potential for use as biodegradable automotive transmission fluids, metal working fluids, steel cold rolling oils, fire resistant hydraulic fluids and for automotive gear oils.

6. Industry study with forecasts for 2012–2017

World lubricant demand will increase 1.6% per year to 40.5 million metric tonnes in 2012. Although growth will be modest in volume terms, value gains will be more substantial as more expensive high performance lubricants are substituted for lower value ones. Increases will be aided by the ongoing expansion of the world motor vehicle park; as well as by a rebound in manufacturing and other industrial activity from the global economic lowdown of 2008 and 2009. Advances will be the strongest in the developing Asian countries due to on going rapid industrialization as well as rising car ownership rates, particularly in China. These trends will also favor growth in the Africa/middle east and Latin America. In contrast, greater availability of high performance lubricants, increased global competition and increasingly stringent environmental regulations will restrain advances or contribute to negative growth in lubricant demand in the more developed countries of Western Europe, the United States and Canada, as well as in the European Union member countries of Eastern Europe and in Japan.

The growth will be led by strong gains in the developing Asian countries due to rapid expansion of the motor vehicle park, particularly in China and India. Healthy growth will also occur in Latin America and the Africa/Mideast region, while advances in Eastern Europe will be below average. The fastest growth in lubricant demand through 2012 will be in manufacturing and other markets. The Asia/Pacific region, led by China, will continue to be the primary driver of growth in these markets due to companies worldwide pursuing the region's key advantages of relatively low labor costs and political stability. Latin America and the Africa/Mideast region will also achieve favorable growth in manufacturing as significant countries in both regions continue their industrial development [67,36] (Shell, Exxon Mobil, BP, Chevron, Petro China, Total, Sinopec, and Lukoil).

7. Future prospects

Current quality trends in lubricants indicate significant shift in viscosity grades and product specifications. In fact the unconventional base oils exceed performance of conventional lubricants in terms of volatility requirement, oxidation stability, low carbon forming tendency, viscosity, stability, and response to additives. The above changes along with environmental conditions have led to significant developments in lubricating oils based oil manufacturing technology. Introduction of smaller, faster, more efficient

equipments operating at higher speeds, temperatures, stresses and pressures favors higher quality lubricants. Freedom from deposits, radiation resistance, greater efficiency, reduced maintenance and larger fluid life are the other possible benefits from using alternative lubricant base stocks. The need for automatic transmission fluids and engine oils, approaching the synthetic in performance, their systematic supply and cost has necessitated the improvement in refiner's ability to economically boost performance. Despite evidences that costs can be cut by switching to synthetic lubricants, the strong counter attack by petroleum lubricant manufacturers/sellers such as Chevron, Conoco, Exxon, Pennzoil and Shell resists the synlube market by providing high quality petroleum base oils [68].

The effectiveness of future higher performance lubricants will, inevitably, depend upon the end user's ability to select the appropriate performance lubricant for his engine and then use and dispose off the product in the correct manner so that the maximum benefit for the engine and the environment can be derived. Lubricating oil has a significant role to play in the reduction of energy losses caused by friction. The environmental aspects are to be discussed of using biodegradable lubricants in friction pairs of ceramic composite to reduce wear rate [69].

A saving of 1–2% in fuel consumption is achievable through the use of an appropriate lubricant. These, however, are generally of a low viscosity designation than the more popular grades of motor oils. The effect that low viscosity oils could have on engine emissions has to be considered (low viscosity oils contain more volatile fluids). Increasingly stringent emission limits are being proposed and set by governments, in consultation with the automotive and oil industries. Changes in engine design and fuel quality have led to greater loads being imposed on the lubricants. The provision for better performance lubricants for even more specific applications itself is a challenge for lubricant industry [70].

Provision of the new generation heavy duty lubricants is an example of the industry responding to the need to lubricate automotive equipment that will itself reduce the environmental loading by reducing emissions and to reach biodegradable and non-toxic [35].

However, this can and will be met through optimization of the performance of engine fuel oil combination. These improvements in product technology represent increased development costs which can only be justified if the products find commercial markets. So the need will grow for much greater emphasis on pack labelling and performance identifications to enable the users to select the appropriate oil for each application, otherwise the potential benefits will not be realized. Test results indicate the possibility to connect the highest performance level with the best biodegradable [71].

It is now widely accepted that synthesized fluids, such as PAOs/ester blends, offer a number of inherent performance advantages over conventional petroleum based oils for the formulation of modern automotive engine oils. Krulish et al. have shown that a blend of PAO and an organic ester provides an excellent base fluid for the formulation of synthesized crankcase oils.

Ester lubricants (such as C36 dimer esters and polyoleates) offer a number of advantages over mineral oils as the lubricant component of 2-stroke engine mixtures. Diesters and phthalates have found their major application as air compressor lubricants and are also used in compressors handling natural gas. Diesters and polyol esters may also be blended with PAOs for use in the various compressor types.

With the phasing out of chlorofluorocarbons (CFCs), owing to their potential ozone-depleting effects, the traditional naphthenic and paraffinic mineral oil currently used in refrigeration lubricants are being replaced by polyol ester oils. The main reason for this is that the traditional mineral oils are not miscible with the more polar hydroflurocarbons (HFCs) which are replacing CFCs. The bulk of aviation lubricant demand is for gas turbine lubricants for both military and civilian use. The first generations of oils (Type 1) were diesters but, over the last 25 years, these have slowly lost ground to the more expensive (Type 2) polyol esters [72].

The requirement for lubricants to operate at high temperature is causing a move away from mineral oil to esters. In particular, due to the better temperature stability of polyols, there is a growing tendency to use these in preference environmental pressure, the chemistry of esters is being modified so as to produce compounds which have high biodegradabilities, low toxicity and clean engine emissions.

The most important requirement of base oils in the fifties was the correct viscosity and the absence of acidic components. Base oils in the sixties were down graded to solvents or carriers for additives. In the seventies, some synthetic fluids with uniform basic chemical structure offered performance superior to that of mineral base oils. But the higher price of these products hindered their market acceptance. In the eighties however, lower price, quasi synthetic hydro cracked oils were introduced in Western Europe which closely matched the properties of synthetic hydrocarbons (Shell, BP, Fuchs). In the nineties base oil developments were influenced by demands on lubricant performance, environmental, health and safety criteria. This led to chemically more pure oils such as hydro cracked products, polyalphaolefins and esters gaining importance. Natural fatty oils and their oleo chemical derivatives have experienced a renaissance because of their rapid biodegradability. The trend towards ever greater performance and even better compatibility continues in the first decade of the new millennium [73].

8. Conclusion

One of the biggest challenges is development of a universal biodegradable base stock that could replace mineral oil base stocks in the new generation of lubricants with the current attention on the environment. Industrial users in parts of the world have began to appreciate that some synthetic lubricants notably those based upon polyesters vegetable and polyalkylene glycols provide cost-effective lubrication in all service conditions, when environmental concerns are recognized as being prime importance.

The need for eco-friendly products has been discussed at length in many forums. ASTM is reviewing the current products available today and the testing required for defining for performance criteria for biodegradable fluids.

From an environmental point of view i.e. rapid biodegradability and favorable ecotoxicological characteristics, a proper selection must be made which combines the previously mentioned favorable characteristics at an acceptable price.

TMP esters, other polyol esters, dicaboxylic acid esters and complex esters form a broad spectrum of possible base oil candidates. The next 10–15 years will be an interesting time, with little or no, or even negative growth for conventional lubricant base oils. So new base fluids based on synthetics have been developed to cater to the needs of high performance lubricants. As a result, synthetic fluids as a base stock have attained considerable importance in a variety of industrial and military applications. Some of the applications include engine lubricants, gear oils, hydraulic oils, compressor oils, pump and turbine oils.

If certain cases of applications require special properties like a power plant needs oil that can tolerate ultra-high temperatures without bursting into flames or a tractor has to startup at low temperatures or the operating environment has a high risk of contamination, synthetic may be the best choice. Some most critical applications of jet turbines or refrigeration units or high performing compressors need some special properties that only a synthetic

can offer and cannot be obtained by mineral oils. Certain synthetic fluid will have to be selected and applied in spite of some of its disadvantageous properties implying that each type of synthetic offers some strong advantages and carries some disadvantages as well.

Order of importance of various lubricant base stocks depends upon type of applications, cost and biodegradability requirements. For applications involving total loss to environment such as lubricants of two stroke systems, open gears, chain saw and bar applications, vegetable oils and their modified derivatives have gained utmost importance. For applications involving quenching, cutting, rolling and metal working polyalkylene glycols and their derivatives, trans esterified esters of vegetable oils and vegetable oils as such are important. Application involving instrument lubrication, high temperature applications, gas turbine aircraft engines and very high speed automotive engines, ester based synthetic lubricants and their blends with highly hydro processed mineral oils are used. Applications involving hydraulic oils, turbine oils, refrigeration oils, synthetic esters, trans esterified vegetable oils, polyalkylene glycol ethers and esters are most favored lubricants. For automotive energy efficient long drain interval lubricant applications, hydro processed mineral oils, some times blended with esters are being increasingly favored. For food processing/medicinal/textile and speciality applications modified trans esterified vegetable oil derivatives have almost entirely replaced white mineral oils. Development of chemically modified esters based on non-traditional biological resources is highly lurative option for environment friendly applications. Development of synthetic esters from cost effective sources for critical applications (automotive and industrial) is one of the best choices. Also, there is a need for the development of hydrocarbon based mineral oils with improved biodegradability and performance.

However, the shift to biodegradable products in the area of hydraulic fluids, chain saw oils, compressor lubricants and metal working fluids is increasing rapidly. Best lubricant technologies are required to improve the regional quality levels for reducing lubricant consumption in the long run. As a result of more and more stringent environmental regulations regarding emission limits, resource conservation and environmental and disposal issues, the lubricants are required to be assessed on the basis of increased thermal and mechanical stress ability, lower consumption, ecological safety and rapid biodegradability. These factors have a direct impact on lubricant consumers and R&D. The forecast for ecofriendly/biodegradable lubricants for next 10–15 years is a worldwide volume share of approximately 15% and in some regions up to 30%. The world lubricant market will have to face a lot of changes within the next 5–10 years and it certainly will remain an interesting field of activity.

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